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AVERAGE ELECTRONEGATIVITY ON SOME APPLICATIONS IN IONIC CONDUCTORS AND OTHER MATERIALS

Masaru Aniya

Department of Physics, Graduate School of Science and Technology-Kumamoto University
Kumamoto 860-8555, Japan
e-mail : aniya@gpo.kumamoto-u.ac.jp

ABSTRACT

AVERAGE ELECTRONEGATIVITY ON SOME APPLICATIONS IN IONIC CONDUCTORS AND OTHER MATERIALS. The average electronegativity is a parameter defined in terms of the electronegativity of the elements and the chemical composition of the compounds. It has been introduced to study the chemical trends of the materials. Previous studies have revealed that the average electronegativity provides an easy and powerful mean to classify and understand many basic properties of materials. In the present report, a brief review on the application of average electronegativity is given. Topics such as ionic conductivity, network expansion, sound velocity and medium range structure in superionic glasses, superconductivity, glass forming ability, correlation with fragility, among other properties are covered. All these examples indicate that the average electronegativity provides a method to predict materials properties from chemical formula of the compounds. Limitations and further extension of the model is mentioned briefly.

Key words : Average electronegativity, Superionic glasses, Ionic conductors, Superconductors

ABSTRAK

ELEKTRONEGATIFITAS RATA-RATA PADA APLIKASI DALAM KONDUKTOR IONIK DAN MATERIAL LAIN. Elektronegatifitas rata-rata adalah sebuah parameter yang didefinisikan dalam istilah sebagai elektronegatifitas dari unsur dan komposisi kimia suatu senyawa. Parameter ini diperkenalkan untuk mempelajari kecenderungan kimiawi suatu material. Penelitian sebelumnya telah menunjukkan bahwa elektronegatifitas rata-rata menyajikan cara mudah dan sangat kuat untuk mengklasifikasi dan memahami banyak sifat-sifat dasar suatu material. Pada makalah ini, akan disampaikan ulasan singkat tentang aplikasi elektronegatifitas rata-rata. Topik pembahasan mencakup berbagai sifat tentang konduktifitas ionik, ekspansi jaringan, kecepatan suara dan struktur kisaran medium dalam gelas superionik, superkonduktifitas, kemampuan bentuk gelas dan korelasi dengan *fragility*. Semua contoh tersebut menunjukkan bahwa elektronegatifitas rata-rata memberikan satu metode untuk memprediksi sifat-sifat material berdasarkan rumus kimia senyawanya. Keterbatasan dan pengembangan lebih jauh dari model tersebut dibahas secara singkat.

Kata kunci : Elektronegatifitas rata-rata, Gelas superionik, Konduktor ionik, Superkonduktor

INTRODUCTION

The properties of the materials are intimately related with their bonding nature. The parameters such as valence, atomic size, electronegativity and ionicity are directly associated with the character of the chemical bond. Thus, the use of these parameters provides a mean for classify and understand many basic properties of materials. Some years ago, the author introduced a parameter that describes the average electronegativity of a compound [1]. For a compound whose chemical formula is written as $A_xB_yC_z$,....., where A, B, C,..... and x, y, z,..... denote the elements and the compositions respectively, the average electronegativity is defined as $\chi_m = (\chi_A^z \chi_B^y \chi_C^z \cdots)^{1/(x+y+z+\cdots)}$ where χ_A, χ_B, χ_C, are the electronegativity values of the elements A, B, C,.... , respectively, calculated from the atomic nodal radii. The defined formula has a generalized expression of the principle of electronegativity equalization [2]. The average electronegativity has been used to study some properties of ion conducting glasses such as conductivity trend, network expansion, relation with the medium range structure, glass formability, etc [1,3-7].

In the present report, with the objective to gain further insights on the method and extend their applicability, a short review on previous studies and new

applications of the average electronegativity to ionic conductors and other materials are presented.

THEORY

Some Applications of the Average Electronegativity

For the last several years, superionic conducting glasses have attracted considerable interest from both academic and applied points of view. Generally, superionic conducting glasses have very complex chemical composition and their properties vary depending on these compositions. Therefore, it will be interesting if we have a method to estimate easily the materials properties from the chemical composition. The average electronegativity mentioned in the Introduction provides such a method [1]. When the measured ionic conductivity of $AgI\text{-}Ag_2O\text{-}M_xO_y$ (M = Mo, Se, W, P, Ge) glasses are plotted as a function of the average electronegativity, a tilted S-shaped curve is obtained for each system of glasses [1]. The inflection point of such curve is denoted by χ_c and σ_c. The scaled behavior of the relationship between the average electronegativity and the ionic conductivity (taken at the temperature $0.8\,T_g$) is shown in Figure 1.

The result shown is striking, because a complex quantity such as ionic conductivity in superionic glasses

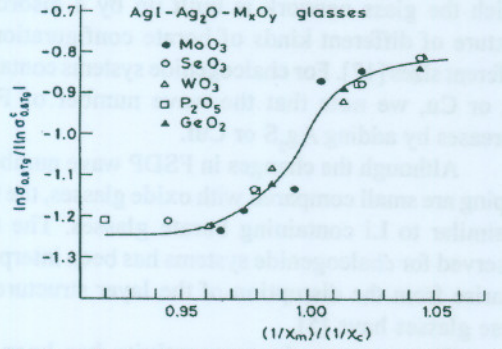

Figure 1. Normalized ionic conductivity as a function of normalized average electronegativity

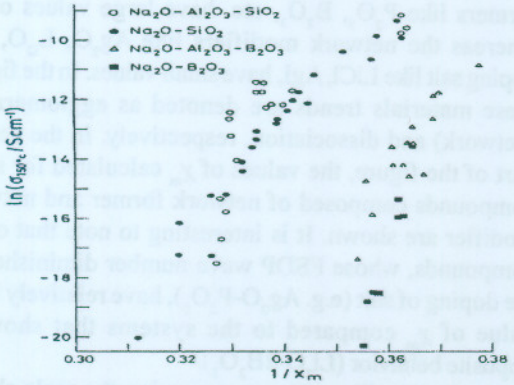

Figure 2. Relationship between the ionic conductivity and the average electronegativity in Na^+ ion conducting glasses

can be scaled using only atomic parameters. This fact opens the possibility that the ionic conductivity in this kind of glasses can be understood from a unified point of view. The relationship between average electronegativity and the activation energy of ion transport, and the glass transition temperature in AgI-containing glasses is reported elsewhere [1]. The background of the result shown in Figure 1 has been discussed [1] using the concept provided by the bond fluctuation model of superionic conductors [8,9]. However, clear physical explanation concerning the origin of the magnitude of χ_c remains to be clarified.

For the sake of comparison, the relationship between average electronegativity and the ionic conductivity in Na^+ ion conducting glasses is shown in Figure 2 [10]. The ionic conductivity data are taken from [11]. Interestingly, for these glasses a tilted S-shaped curve as observed in AgI-containing glasses is not obtained. Instead, we note that glasses based on SiO_2 and B_2O_3 follow different curves. This behavior indicates that in these glasses, the network forming entity dominates the bonding nature which is described by χ_m. The addition of network modifier and salt change gradually the values of χ_m and ionic conductivity. The physical origin of the difference between Ag^+ and Na^+ ion conducting glasses arises from the different nature of chemical bonding that these ions exhibit. This observation is also reflected in the ability of glass formation that will be shown later.

Figure 3 shows the relationship between the sound velocity and the average electronegativity in $AgI\text{-}Ag_2O\text{-}B_2O_3$ glasses. The sound velocity data are taken from [12]. It is noted that the sound velocity changes continuously with χ_m. The data with high values of $1/\chi_m$ correspond to AgI-rich glasses. A peak in the sound velocity value is observed when $1/\chi_m \cong 0.36$. This means that glasses with chemical composition having this value of χ_m are rigid.

Some years ago, a scaling relationship between the ionic conductivity enhancement and the network expansion induced by salt doping in superionic glasses was found by Swenson and Börjesson [13]. From

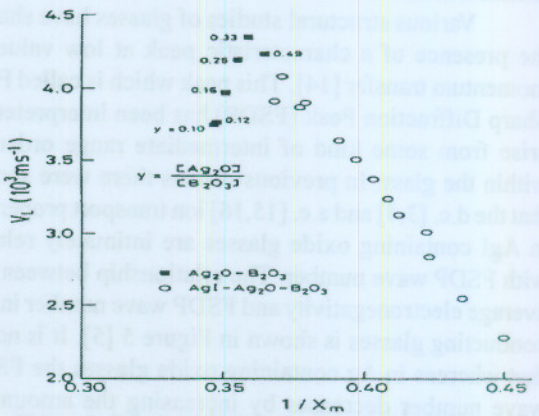

Figure 3. Relationship between the sound velocity and the average electronegativity

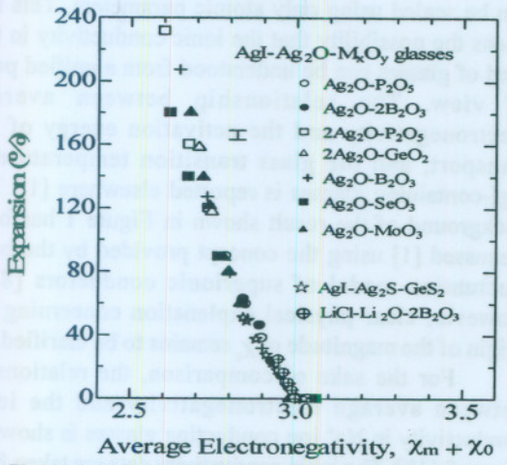

Figure 4. Relationship between the network expansion and average electronegativity. χ_0 is a constant quantity introduced to put all the data on a single curve

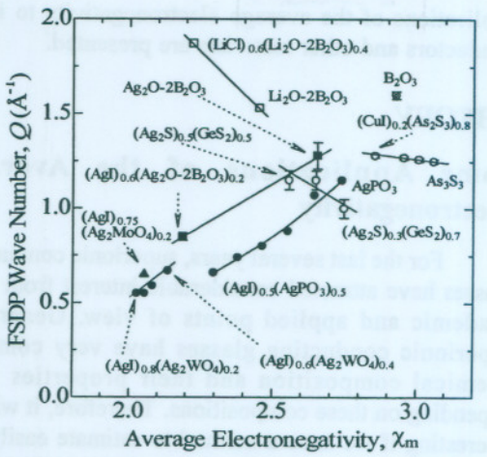

Figure 5. Relationship between the FSDP wave number and the average electronegativity in some oxide and chalcogenide glasses. The lines are drawn as guides for the eyes

this finding they concluded that the available free volume in the glass is the key parameter determining the increase of the ionic conductivity.

In Figure 4, the relationship between the network expansion defined as $Exp = (V_d - V_m)/V_m$ and the average electronegativity in some ion conducting glasses with chemical formula AgI-Ag_2O-M_xO_y is shown. Here, V_m is the molar volume of M_xO_y in Ag_2O-M_xO_y glasses and V_d is the molar volume of M_xO_y in AgI-Ag_2O-M_xO_y glasses. In Figure 4, the results of a Li ion conducting glass and a chalcogenide glass are also included for comparison. The result indicates that the network expansion and the average electronegativity of different glasses collapse onto a single curve if we add a constant quantity χ_0 to each system of glasses. χ_0 is a quantity that depends on the glass system but does not depend on the amount of salt doping [3]. The figure indicates that the network expansion depends only on how much χ_m is modified by salt doping. By making connection with the finding of [13], the increase of the ionic conductivity by salt doping is accompanied by the change in χ_m of the glasses [3]. It should be noted that all the above correlations provide a simple method to predict the materials properties from chemical formula.

Various structural studies of glasses have shown the presence of a characteristic peak at low value of momentum transfer [14]. This peak which is called First Sharp Diffraction Peak (FSDP) has been interpreted to arise from some kind of intermediate range ordering within the glass. In previous studies there were shown that the d.c. [3,4] and a.c. [15,16] ion transport properties in AgI containing oxide glasses are intimately related with FSDP wave number. The relationship between the average electronegativity and FSDP wave number in ion conducting glasses is shown in Figure 5 [5]. It is noted that whereas in Ag containing oxide glasses the FSDP wave number decreases by increasing the amount of AgI, in Li containing oxide glasses, it increases with the concentration of LiCl. This difference in behavior is likely to arise from the different ionic-covalent characters of Li and Ag ions. Due to its covalent character, Ag cross-links the different segments of the network, originating the observed intermediate range ordering.

On the other hand, the larger ionic character of the Li ions makes such cross linking weaker and less directional, which results in the fragmentation of the network. This picture is consistent for instance, with a structural model of LiCl containing borate glasses, in which the glass network is built up by a disordered mixture of different kinds of borate configurations of different sizes [17]. For chalcogenide systems containing Ag or Cu, we note that the wave number of FSDP increases by adding Ag_2S or CuI.

Although the changes in FSDP wave number by doping are small compared with oxide glasses, the trend is similar to Li containing borate glasses. The trend observed for chalcogenide systems has been interpreted to arise from the disruption of the layer structure that these glasses have [5].

The average electronegativity has been also applied to systematize the glass forming ability of the materials [5]. From Figure 6 it is noted that network formers like P_2O_5, B_2O_3, etc. have large values of χ_m, whereas the network modifiers like Ag_2O, $L_{i2}O$, and doping salt like LiCl, AgI, have small values. In the figure, these materials trends are denoted as agglomeration (network) and dissociation, respectively. In the central part of the figure, the values of χ_m calculated for some compounds composed of network former and network modifier are shown. It is interesting to note that oxide compounds, whose FSDP wave number diminishes by the doping of salt (e.g. Ag_2O-P_2O_5), have relatively large value of χ_m compared to the systems that show an opposite behavior (Li_2O-$2B_2O_3$).

Further discussions concerning the scale shown in Figure 5, together with some predictions of materials properties are given in [5].

The results shown above were restricted mainly to ion conducting glasses. In the following, the application of the average electronegativity to other materials are shown. The first example concerns the application to superconductors. Figure 6 shows the relationship between χ_m and the transition temperature to the superconducting state. It is noted that the value of χ_m for most of the known superconductors that include elements, intermetallics and oxides are limited roughly between 1.4 and 2.5 [18]. In particular, the behavior exhibited by oxide superconductors is remarkable. This behavior reveals the importance of the chemistry in the appearance of the phenomena of superconductivity.

The concept of fragility has been used widely to classify and understand the properties of supercooled liquids [19]. Fragility is defined as inverse temperature derivative of the viscosity in Equation (1)

$$F = R\partial \ln \eta / \partial (T_g / T) \quad \text{..... (1)}$$

Where :

R = Gas constant and

T_g = Glass transition temperature

It provides a measure of the phenomenology of structural relaxation. Figure 7 shows the relationship between fragility and average electronegativity. The data of fragility were taken from [20-22]. The gross trend indicates that the fragility increases with the decrease of the average electronegativity. However, Figure 7 indicates that the relation between these two quantities is more complex. Concerning the composition dependence of the fragility, many studies have shown that its variation with the composition is not monotonous [23-25].

According to the bond strength-coordination number fluctuation model of the fragility, the relaxation behavior arises from the interplay between bond connectivity and its disruption of the structural units [26]. The result shown in Figure 7 suggests that the present definition of the average electronegativity

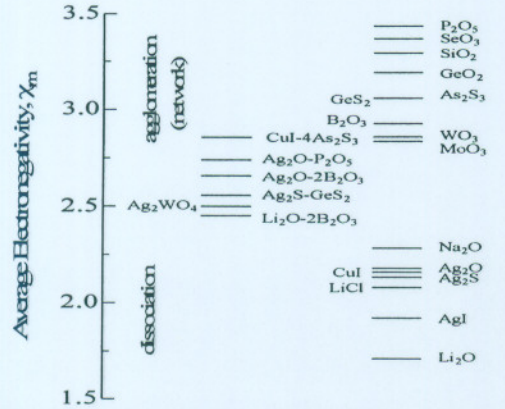

Figure 6. Calculated values of the average electronegativity for some compounds

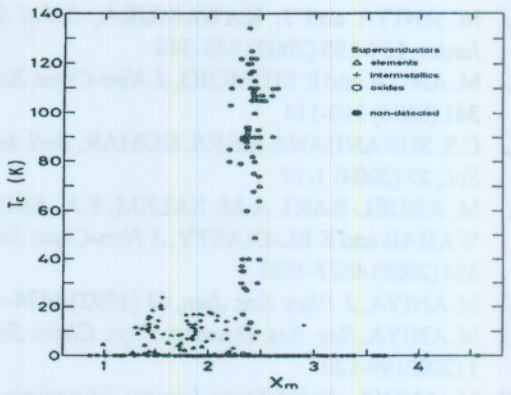

Figure 7. Relationship between the transition temperature to the superconducting state Tc and the average electronegativity.

needs some improvements to study the relationship with quantities such as fragility.

In the literature, different kinds of average electronegativities have been defined and used [27-31]. All of them have the same objective to our model described here. That is, describe and predict in a simple way the materials properties. In order to improve the method and extend its applicability, it will be interesting to compare how these different average electronegativities are interrelated.

CONCLUSION

The chemical bonding related atomic parameters such as valence, atomic size, electronegativity and ionicity provides a mean for classify and understand many basic properties of materials. In the present report, a short review on applications of average electronegativity introduced by the author was given. The result showed that the average electronegativity provides an efficient method to predict materials properties from chemical formula of the compounds. Limitations and further possible extension of the model has been mentioned briefly.

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